Future requirements in ISOTC/158 for high-accuracy gravimetry in support of monitoring levels of greenhouse gases

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ENV52 Stakeholder Workshop

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ISO/TC158 Standards

- ISO 6142-1:2015 Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures

- ISO 19229:2015 Gas analysis — Purity analysis and the treatment of purity data

Governing principles ISO 6142

- Assumption that sampled composition matches prepared composition
- Mixture composition is stable

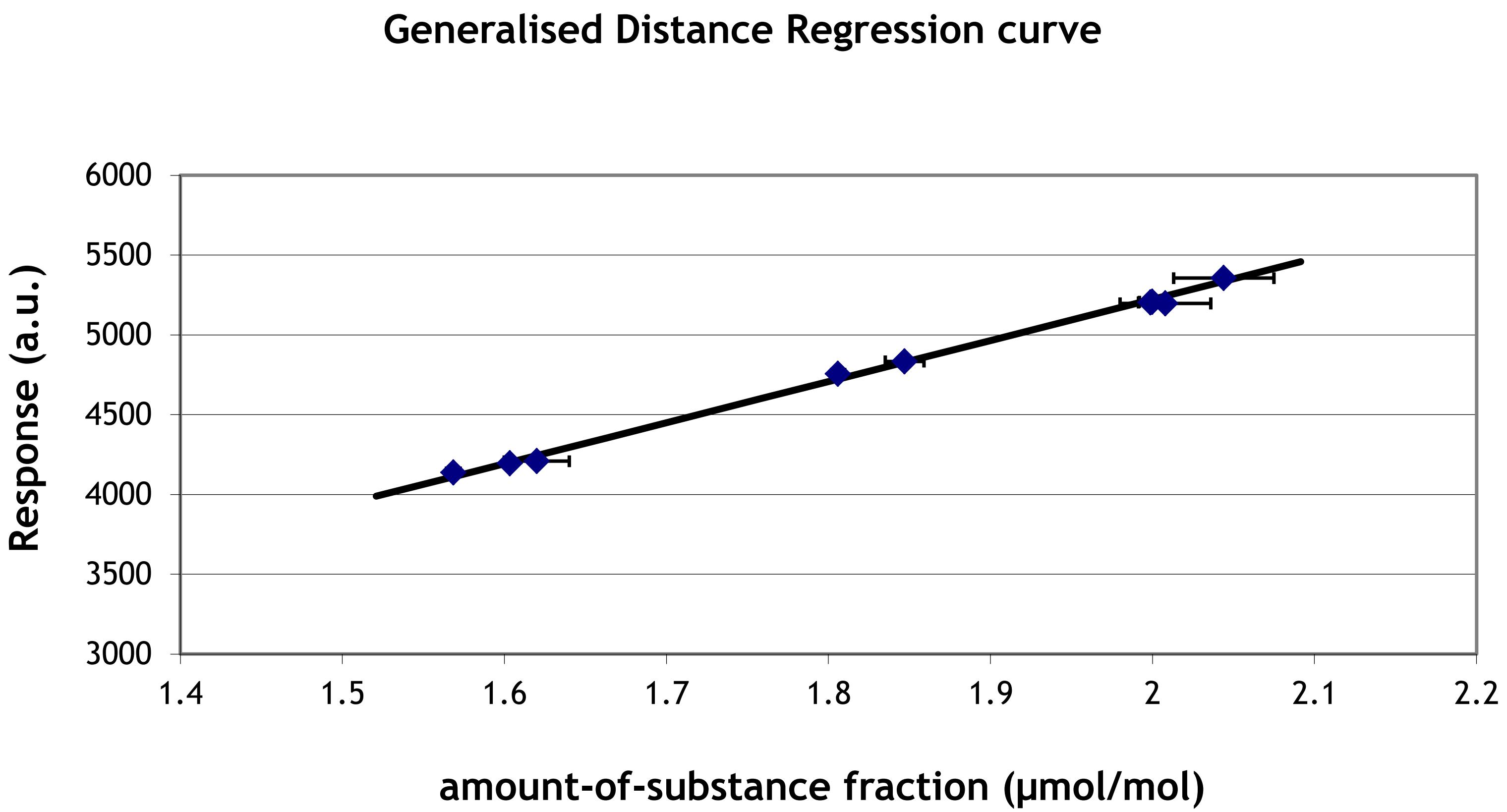
$$x_{i,prep}(t) = \boxed{x_{i,grav} + \Delta x_{i,purity}} + \boxed{\Delta x_{i,stab}(t)} + \boxed{\Delta x_{i,nr}}$$

Current ISO 6142:2001
New ISO 6142-1:2015

Initial losses due to reactions, adsorption

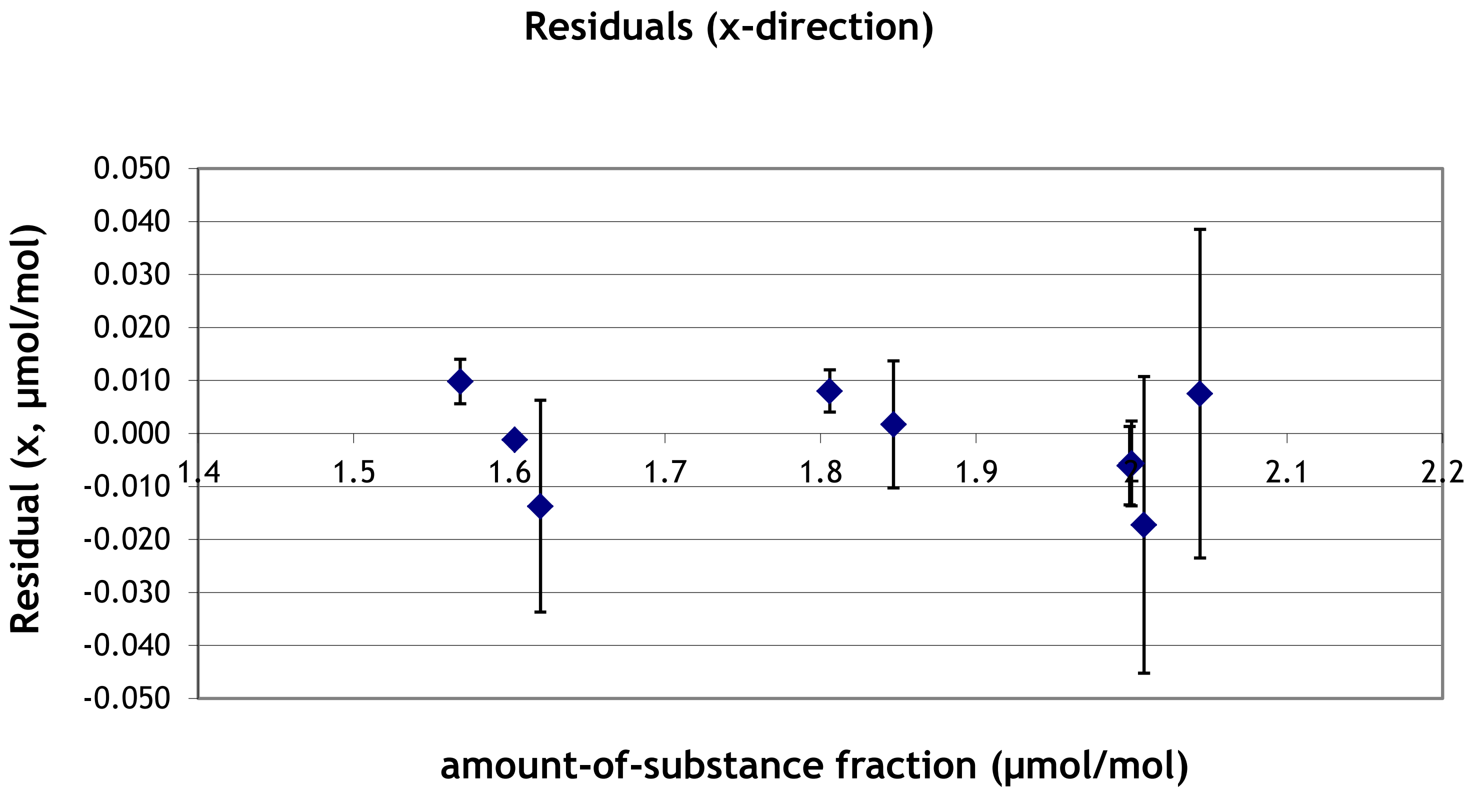
Van der Veen A.M.H., Cox M.G., "Degrees of equivalence across key comparisons in gas analysis", Metrologia **40** (2003), pp. 18-23

Effects of purity analysis: methane in synthetic air



Van der Veen A.M.H., et.al. "International comparison CCQM-P41 Greenhouse gases. 2. Direct comparison of primary standard gas mixtures", Metrologia **44** (2007), TS. 08003

Effects of purity analysis: methane in synthetic air



Measurement model of ISO 6142

- Standard for preparing gravimetric gas mixtures
- Basic model

$$y_k = \frac{n_k}{n_{mix}} = \frac{\sum_{j=1}^{p} \left\{ \frac{x_{kj} m_j}{\sum_{i=1}^{q} x_{ij} M_i} \right\}}{\sum_{j=1}^{p} \left\{ \frac{m_j}{\sum_{i=1}^{q} x_{ij} M_i} \right\}}$$

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Standard uncertainty of an amount–of–substance fraction

- ISO 6142 states expression as follows …

$$u^2(y_k) = \sum_{i=1}^{n} \left\{ \frac{\partial y_k}{\partial M_i} \right\}^2 u^2(M_i) + \sum_{j=1}^{p} \left\{ \frac{\partial y_k}{\partial m_j} \right\}^2 u^2(m_j) + \sum_{A=1}^{p} \sum_{i=1}^{q} \left\{ \frac{\partial y_k}{\partial x_{ij}} \right\}^2 u^2(x_{ij})$$

- where usually the variables on the right-hand side are assumed to be mutually independent

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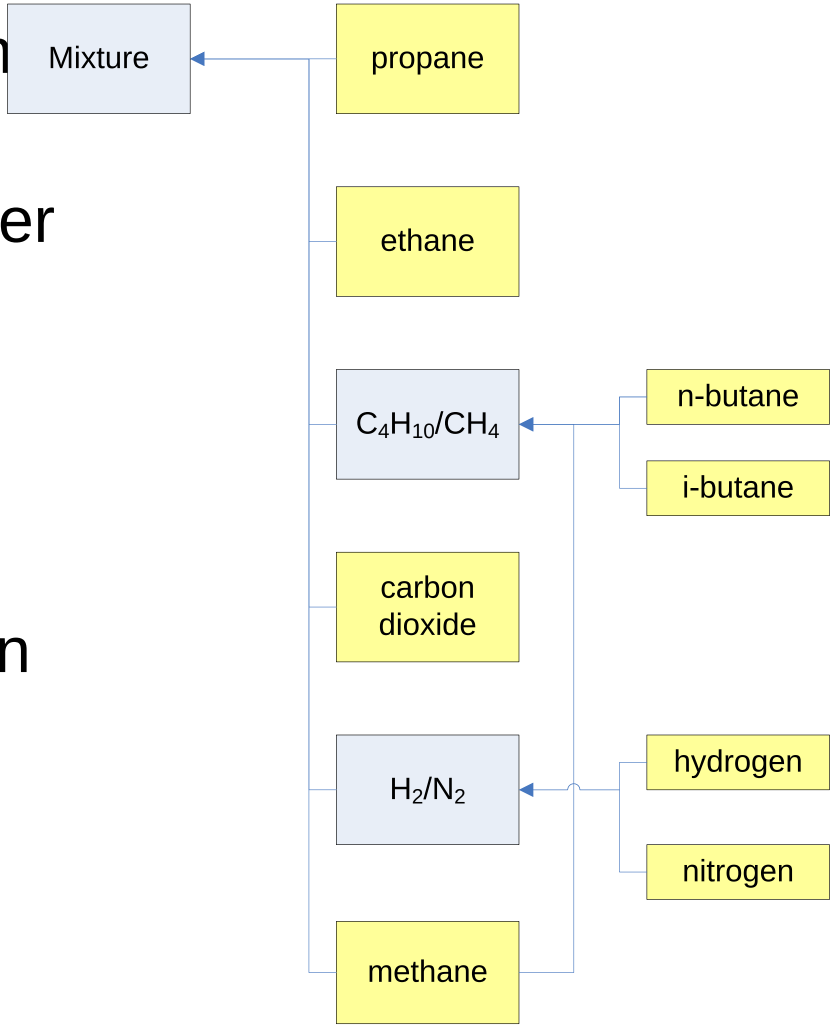
Evaluation of measurement uncertainty

1. Model in ISO 6142 is non-linear
   – Requires validation of using the LPU
2. Output assumed to be Gaussian/*t*-distributed (“$k = 2$”)
   – Requires validation
3. Molecular weights assumed to have negligible uncertainty
   – Validated, but statement is incorrect
4. Input variables can be treated as independent
   – Is not correct, requires validation

Test case: synthetic hydrogen-enriched natural gas mixture

- Multistage preparation
- Combination of high-purity gases, and lesser pure liquids (butanes)
- Use of GUM-S2
- Standard atomic weights of 2009
- All calculations done in MS Excel 2003/2007



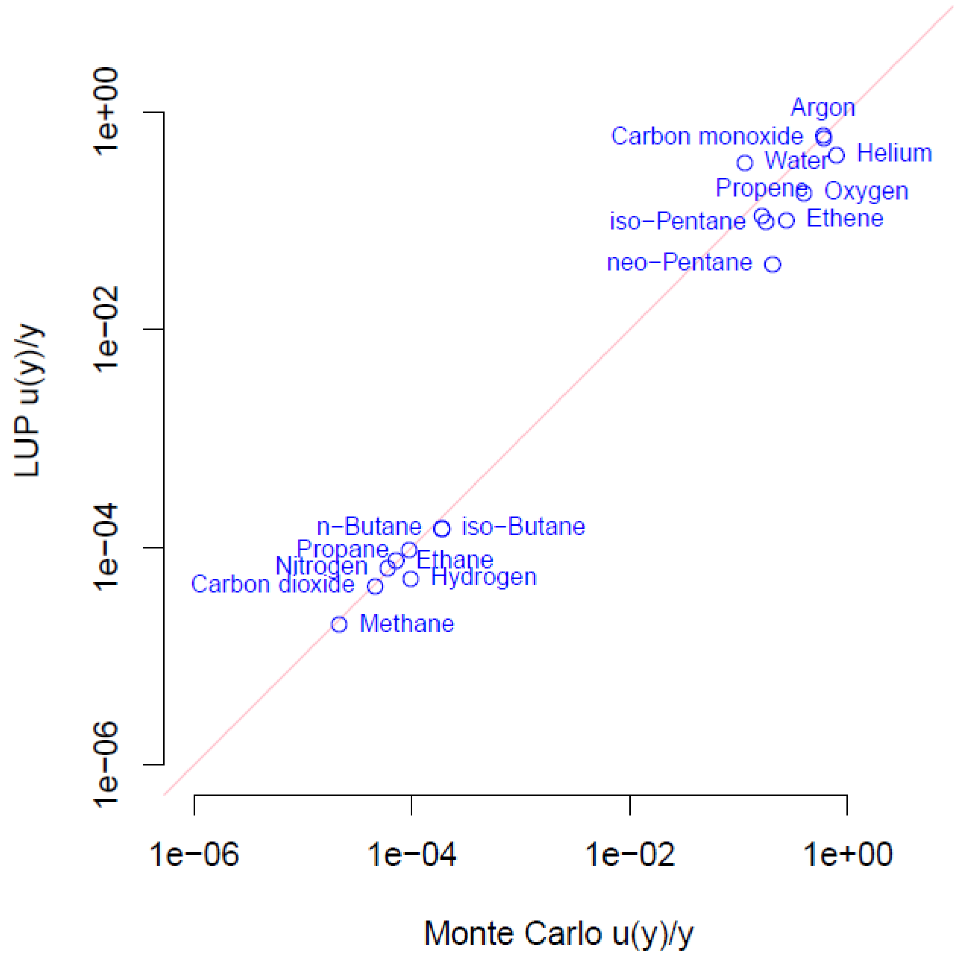
Uncertainty budget natural gas

- For many components, molecular weights as critical as weighing
- For butanes, purity is dominant

Component	y	u(y)	weighing	mol. weight	purity
Methane	0.58895911	0.00001407	0.00000979	0.00000681	0.00000577
Carbon dioxide	0.08910627	0.00000452	0.00000355	0.00000195	0.00000138
Ethane	0.05937309	0.00000449	0.00000434	0.00000077	0.00000090
Propane	0.03212402	0.00000302	0.00000289	0.00000044	0.00000078
Butane	0.00090261	0.00000025	0.00000009	0.00000001	0.00000023
Methyl propane	0.00089891	0.00000025	0.00000009	0.00000001	0.00000023
Hydrogen	0.14912099	0.00000864	0.00000672	0.00000435	0.00000413
Nitrogen	0.07950707	0.00000903	0.00000358	0.00000232	0.00000755

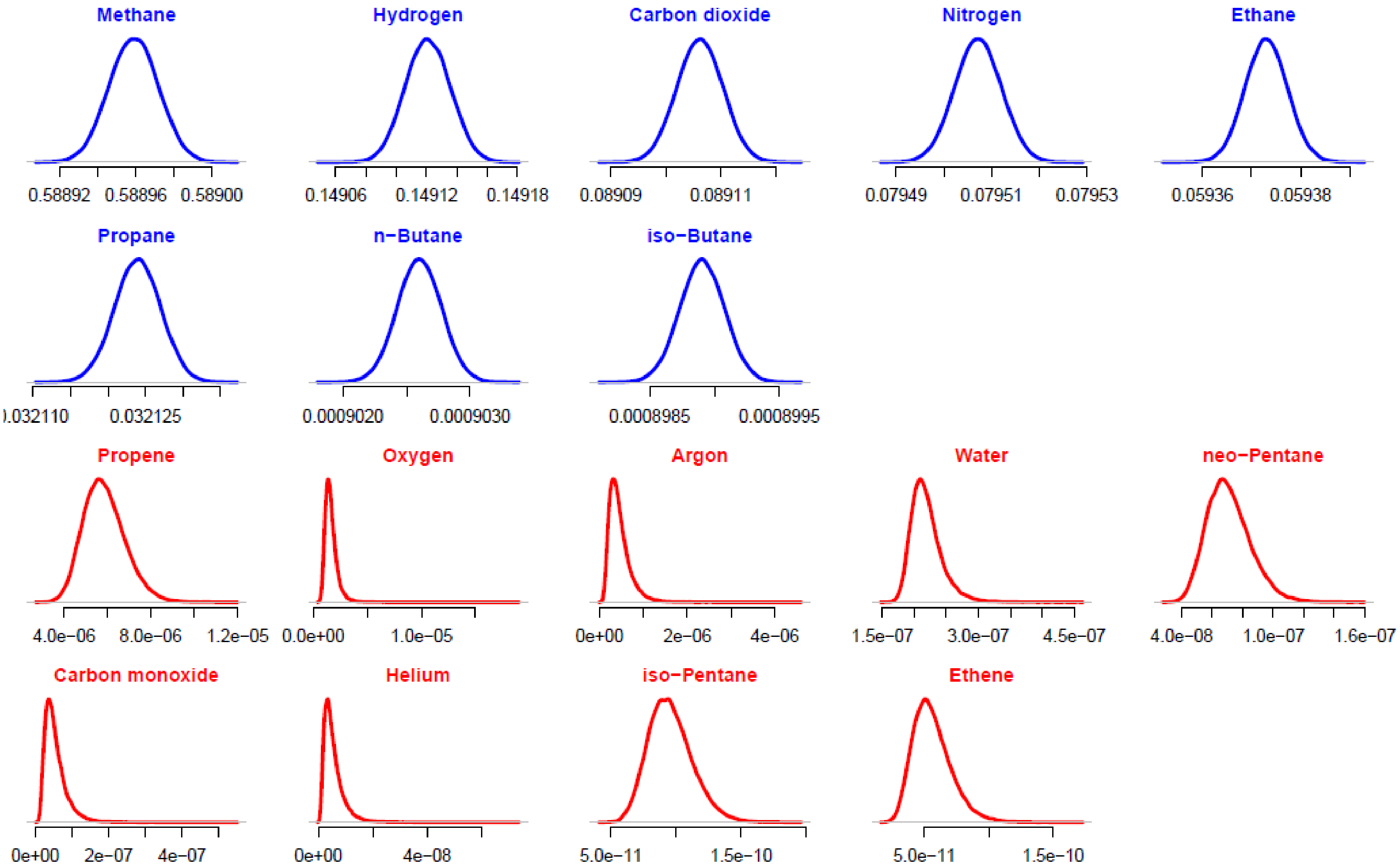
Van der Veen A.M.H., Hafner K., “Atomic weights in gas analysis“, Metrologia **51** (2014), pp. 80-86

LPU versus Monte Carlo

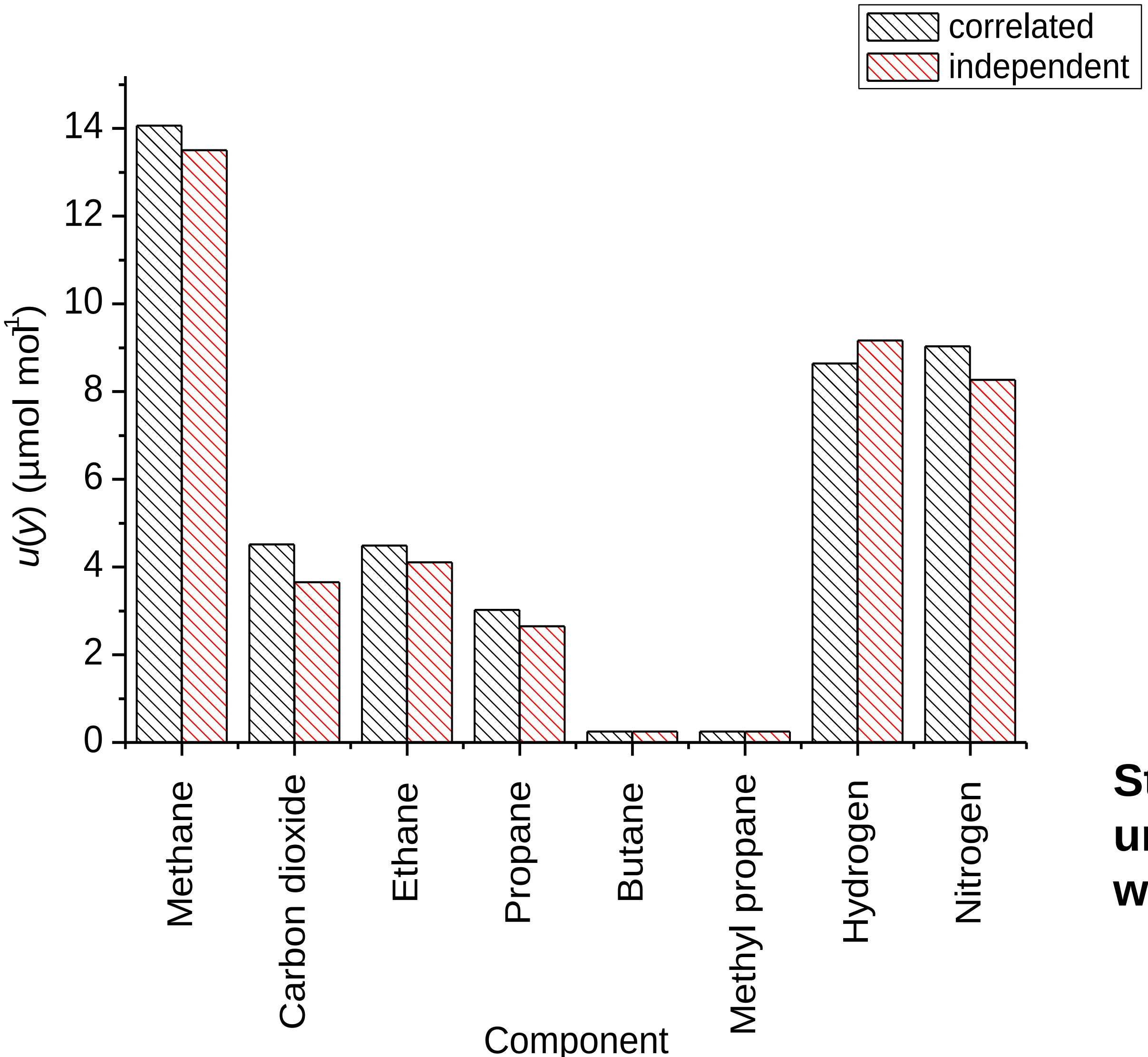


Van der Veen A.M.H., Possolo A., "Comparing the methods of the GUM Supplement 2 to evaluate the uncertainty associated with mixture compositions", in preparation

Output PDFs ISO 6142

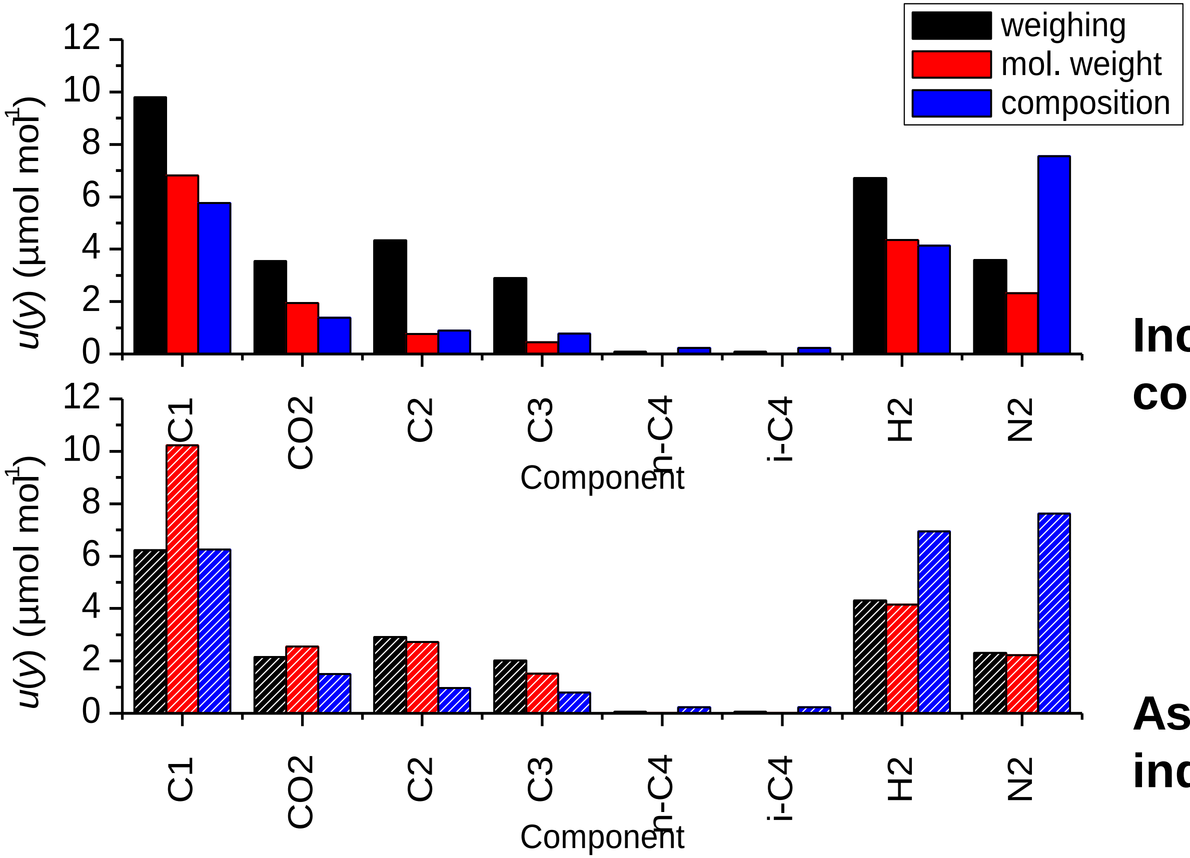


Do correlations matter?



Standard uncertainty weighing 2 mg

Seemingly not, but uncertainty budget tells a different story …

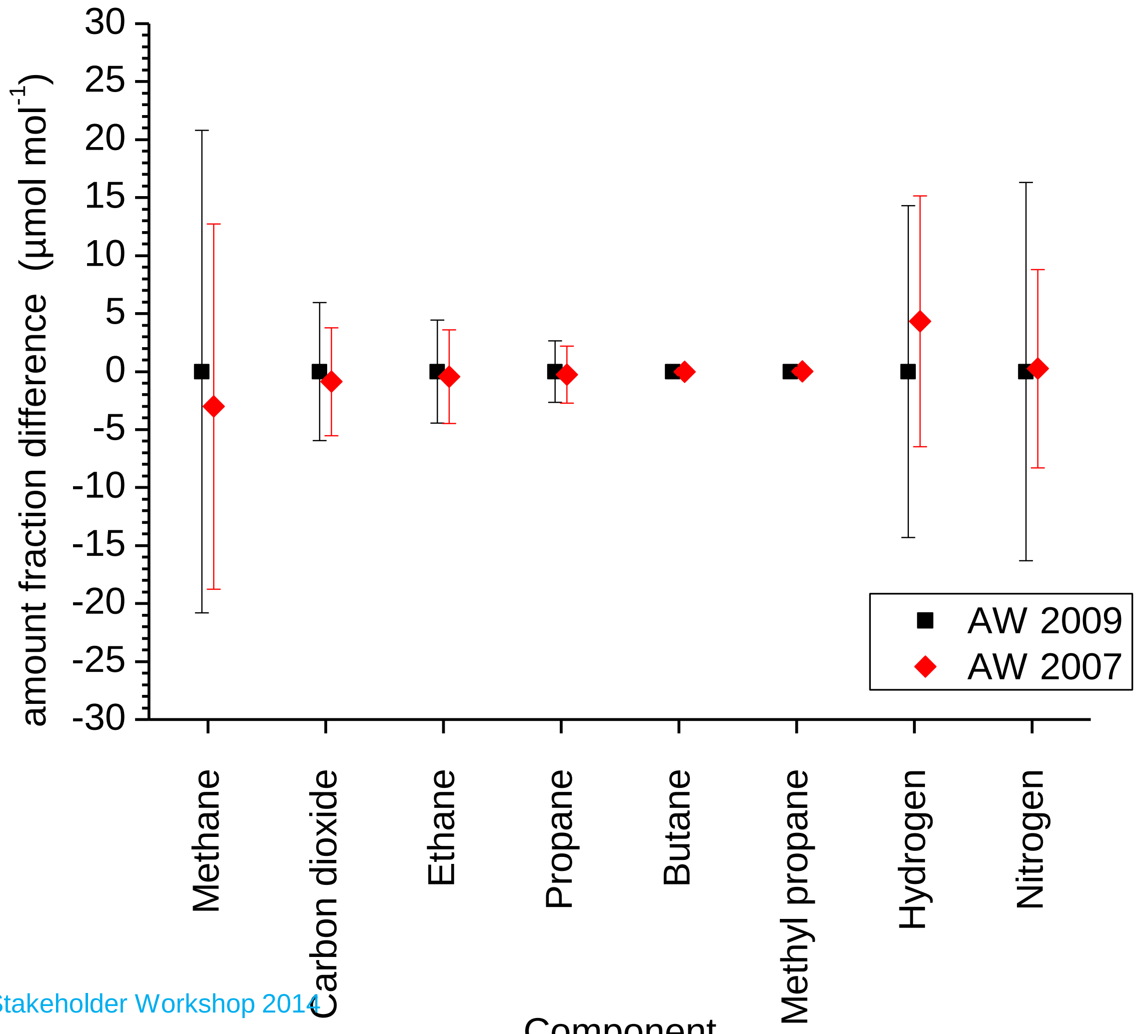


Including correlations

Assumed independence

Van der Veen A.M.H., "Impact of the uncertainty structures of the input data on the accuracy of the calculated composition in gravimetric gas mixture preparation", in preparation

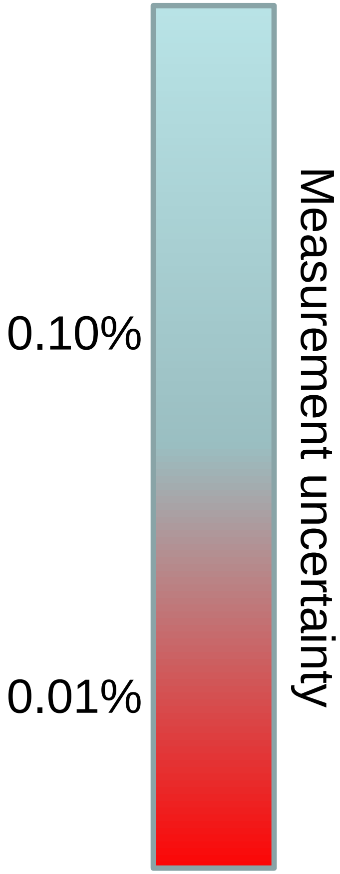
Differences in calculated composition of hydrogen-enriched natural gas

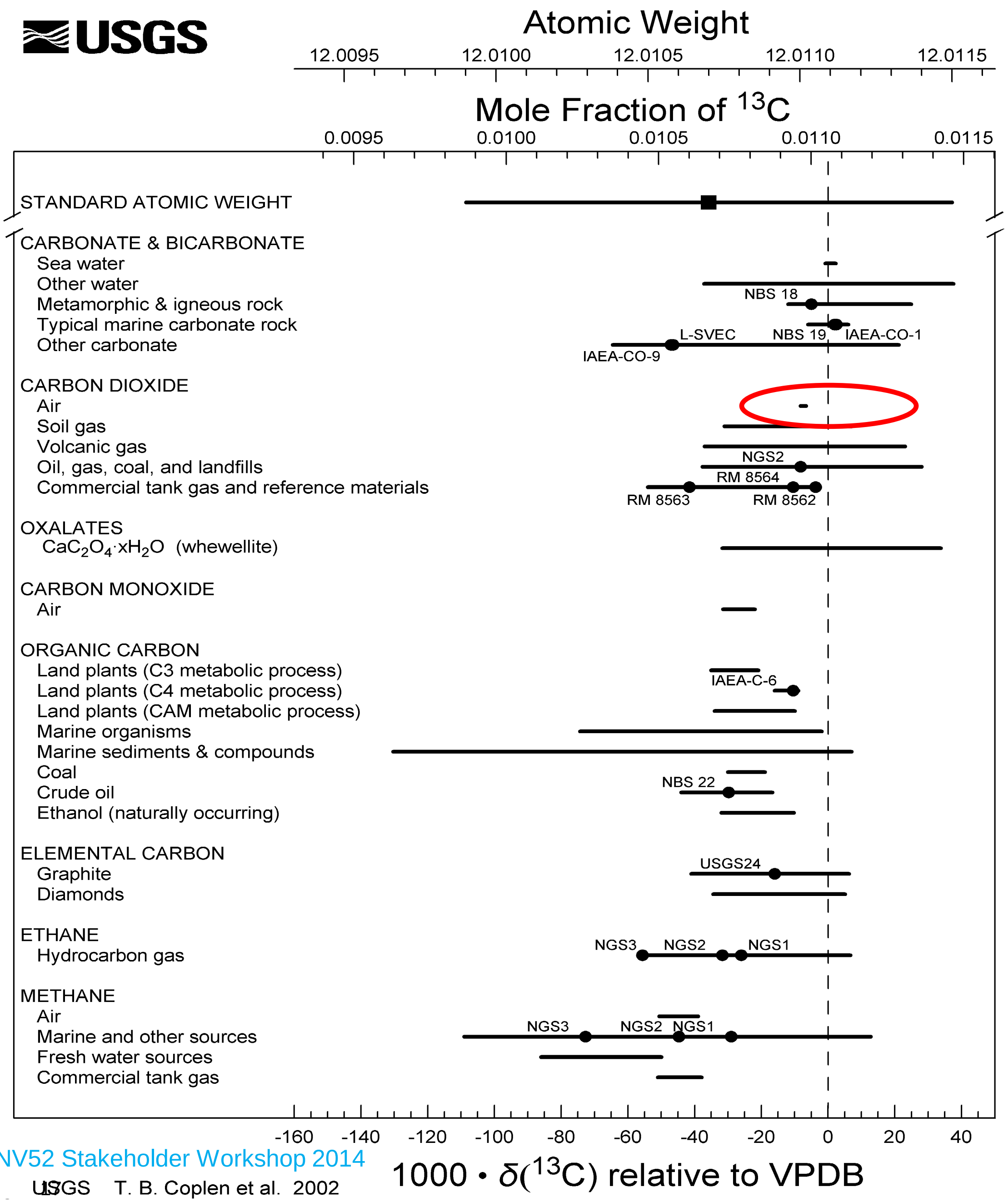


Where is the impact?

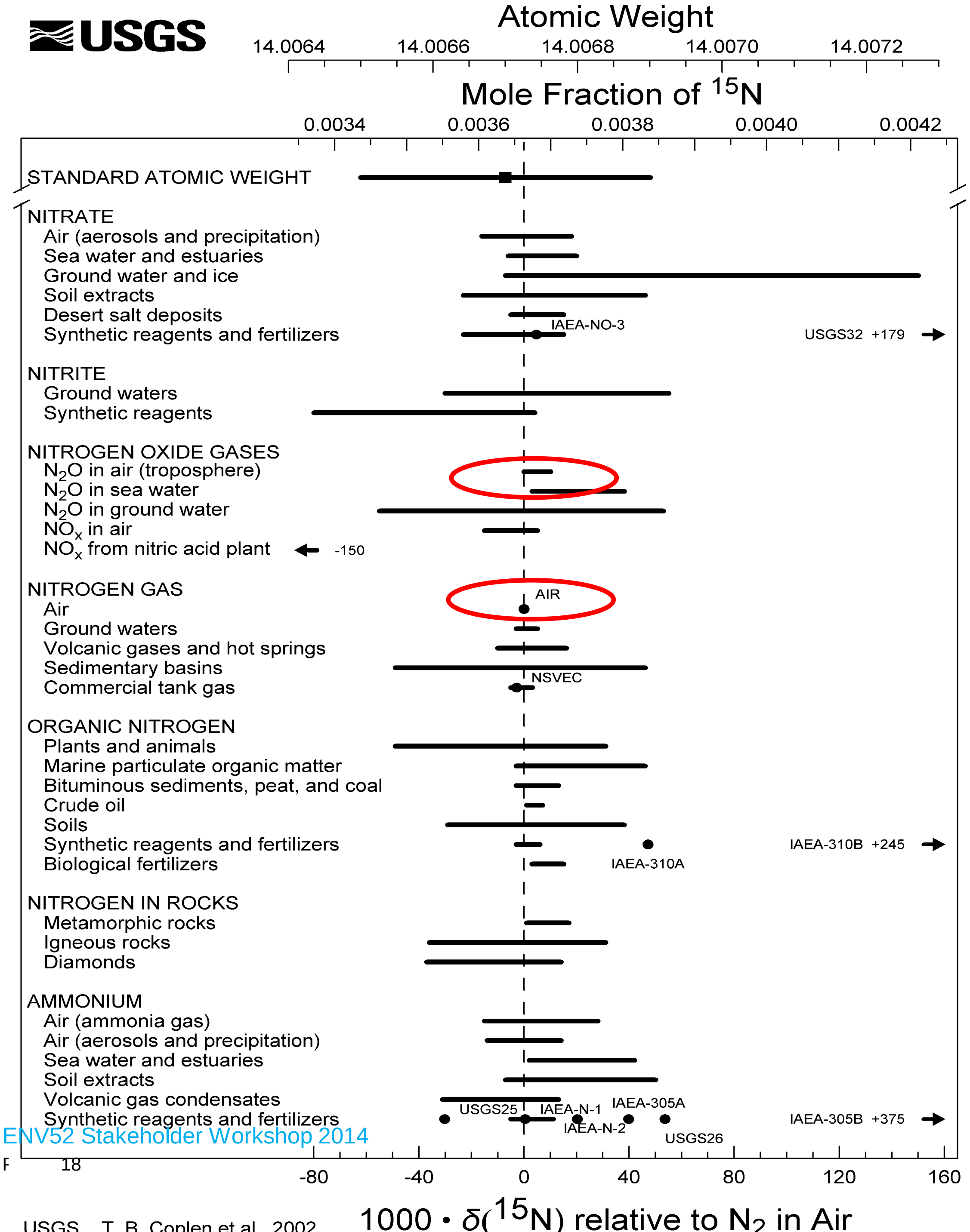
- Mixtures of very pure gases (grade 5.0 or higher)
- Highly accurate gravimetry

- Differences in isotopic composition create issues in
  - Mass spectrometry
  - spectroscopy





USGS T. B. Coplen et al. 2002



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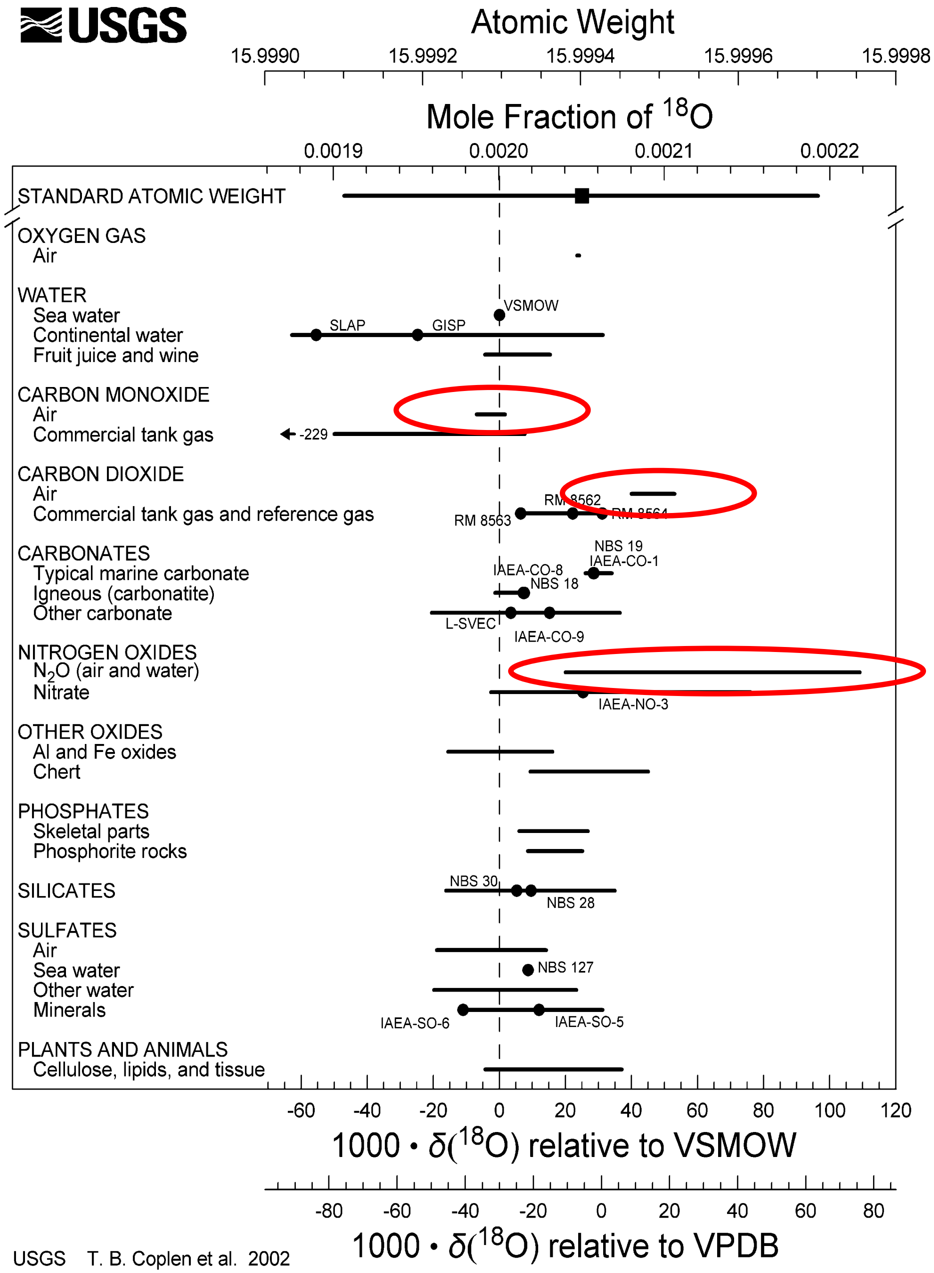
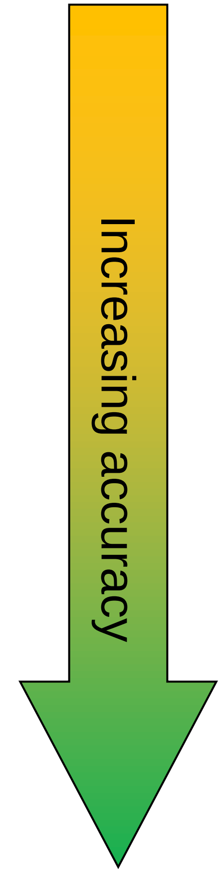

USGS
Atomic Weight
15.9990
15.9992
15.9994
15.9996
15.9998
Mole Fraction of 18O
0.0019
0.0020
0.0021
0.0022
STANDARD ATOMIC WEIGHT
OXYGEN GAS
Air
WATER
Sea water
Continental water
Fruit juice and wine
VSMOW
SLAP
GISP
CARBON MONOXIDE
Air
Commercial tank gas
-229
CARBON DIOXIDE
Air
Commercial tank gas and reference gas
RM 8562
RM 8563
RM 8564
CARBONATES
Typical marine carbonate
Igneous (carbonatite)
Other carbonate
NBS 19
IAEA-CO-1
IAEA-CO-8
NBS 18
L-SVEC
IAEA-CO-9
NITROGEN OXIDES
N2O (air and water)
Nitrate
IAEA-NO-3
OTHER OXIDES
Al and Fe oxides
Chert
PHOSPHATES
Skeletal parts
Phosphorite rocks
SILICATES
NBS 30
NBS 28
SULFATES
Air
Sea water
Other water
Minerals
NBS 127
IAEA-SO-6
IAEA-SO-5
PLANTS AND ANIMALS
Cellulose, lipids, and tissue
-60 -40 -20 0 20 40 60 80 100 120
1000 • δ(18O) relative to VSMOW
-80 -60 -40 -20 0 20 40 60 80
1000 • δ(18O) relative to VPDB
USGS T. B. Coplen et al. 2002

Values and uncertainties for atomic weights

- Use of standard atomic weights
  - Interpretation using the rectangular distribution
- Use of delta scale intervals when the source(s) of the element are known
- Use of the isotopic composition and masses of the isotopes
  - Most accurate and laborious
  - Work also for isotopically enriched or depleted materials



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IUPAC Guidelines

- Development of a harmonised approach to calculating and using atomic and molecular weights
- Collaboration between members of the CIAAW and JCGM WG1
- Project develops two documents
  - General guidelines
  - Statistical and metrological backgounds
- Draft papers expected by the end of 2014

Concluding remarks

- TC158 standards provide a suitable framework for getting started with high-accuracy greenhouse standards
- Work is to be done with respect to
  - Improved purity analysis
  - Assessing the fraction non-recoverable in gas mixture preparation
  - Reference molecular weight for the constituents in air
  - Validating the uncertainty calculations